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(56) Documents considered for evaluation of  
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US 53 89 710 A  
US 53 69 154 A  
US 53 08 894 A  
EP 05 51 687 A1  
WO 96 31 568 A1  
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WP 99 47 605 A1

The following details were derived from the documents submitted by the applicant

(54) [Title of the Invention]: **Calenderable Polyester Mixture**

(57) [Abstract] The invention relates to a polyester mixture that can be processed on calenders for the production of polyester films, sheets, and coatings. A calenderable polyester mixture is already known. This has the drawback that, during processing on calenders, bank<sup>TN1</sup> formation of the thermoplastic melt is often insufficient so that the quality of the finished product is adversely affected. The underlying issue of the invention is to provide a calenderable polyester mixture whose plasticized melt possesses good elongation and flow properties and therefore permits formation of a homogeneous rolling bank in the roll nip with the objective of producing high-grade polyester sheets and minimizing production disturbances. This objective can surprisingly be solved by means of adding a modifier based on core-shell copolymers to the polyester mixture, in addition to the additives to reduce adhesion. The modifier to adjust flow properties, viscosity and bank formation of the thermoplastic melt is methacrylate-butadiene-styrene

or methacrylate-butyl acrylate core-shell polymer added to the polyester mixture in an amount of 5 to 40 wt%, in reference to the total weight. An amorphous polyester polymer that can be processed below 240°C is then used as polyester. A situation is achieved by means of this in which a properly rolling homogeneous bank is formed in the roll nip.

<sup>TN1</sup> Translator's Note: this is also referred to as "bead" formation.

### Description

[0001] The invention relates to a polyester mixture for processing on calendering equipment for the production of polyester films, sheets, and coatings (subsequently referred to as polyester films).

[0002] The production of film, sheets, and coatings made of plastics, like PVC and other thermoplastics, on calendering machines is known. For this purpose, the plastics are mixed with specific additives, like stabilizers to prevent thermal degradation, modifiers for transparency, heat stability or opacity, pigments, lubricants and processing auxiliaries, antistatic agents, UV stabilizers, flame retardants and others. The mixed ingredients are plasticized in a kneader or extruder. The dry powder is melted by means of heat, shear and pressure and then sent to the heated rolls of the calendering line (EP 0744439 A1).

[0003] Attempts to process polyester into films on the very effective calendering machine have not yielded adequate success, since the sometimes inadequate melt strength of the polyester and/or tendency of the polyester polymer toward crystallization meant that a nonhomogeneous mass was formed that could not be processed on calenders and also adhered to the calender rolls. A polyester mixture suitable for processing on calendering equipment was proposed as an alternative for the production of polyester rolls by means of extrusion methods (WO-PS 99/47605). This polyester mixture consists of a polyester that has a crystallization half-life in the molten state of at least 5 minutes and an additive to prevent adhesion of the polyester to the calender rolls. The polyester consists essentially of a dicarboxylic acid component chosen from terephthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, isophthalic acid or their mixtures and at least 80 mol% of a diol component, chosen from diols containing 2 to about 10 carbon atoms and their mixtures.

[0004] The additives to prevent sticking are mixed with the polyester in an amount from 0.01 to 10 wt% in reference to the weight of the polyesters. Internal lubricants, slip agents or their mixtures are used as additives. They can be fatty acid amides, metal salts of organic acids, fatty acids and esters, hydrocarbon waxes, chemically modified polyolefin waxes, ester waxes, glycerol mono- and distearates, talc and acrylic copolymers. In addition to these additives, other

modifiers, like antioxidants, stabilizers, crosslinking agents and others, can also be used. The known calenderable polyester mixture has the deficiency that, instead of a properly rolling a uniform bank, a folding, peaking or undulating bank is formed during processing on calenders in the input region of the thermoplastic polyester melt between the roll pairs. This is possibly due to the fact that the melt plasticized from the polyester mixture, including the employed additives and modifiers, does not always have the required elongation and flow properties as a function of the mixing and thermal processes. In addition to that, the melt still executes a wave motion in the direction of the roll edge, in addition to the rotational motion forming in the roll nip, and overlapping of the flow conditions or partial reversal of the flow direction occurs because of the high pressure prevailing in the roll nip. The flow conditions cause not only agitation and shear of the melt, but also adversely affect the surface of the melt bank. This nonuniform, nonhomogeneous bank adversely affects thickness uniformity and the structure of the films in the longitudinal and transverse direction and therefore the quality of the finished product. In cases of more severe limitations of the rolling capability of the bank, disturbances appear, which can be compensated by adjusting the roll speed, but also lead to quality deficiencies. In the extreme case the rolling capability of the bank can be so restricted that an interruption of the calendering process is necessary and the polyester mixture being processed must be readjusted.

[0005] The objective underlying the invention is therefore to provide a calenderable polyester mixture whose plasticized melt has good elongation and flow properties and permits the formation of a homogenous, uniform, well-rolling bank in the roll nip with the objective of producing high-grade polyester films on calendering equipment and minimizing production disturbances.

[0006] This problem can surprisingly be solved by means of adding to the polyester mixture a modifier based on core-shell copolymers in addition to the additives to reduce adhesion and antioxidants in order to prevent oxidation of the melt on the rolls.

[0007] The calenderable polyester mixture contains

- a) a polyester based on at least 80 mol% of a dicarboxylic acid component, chosen from terephthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, isophthalic acid or their mixtures and at least 80 mol% of a diol component, chosen from

diols having 2 to 10 carbon atoms and their mixtures, the polyester having a crystallization half-life in the molten state of at least 5 minutes,

- b) an additive to reduce adhesion of the polyester, like lubricants, slip agents and antioxidants,
- c) a crosslinking agent and
- d) additional modifiers and conventional additives,

characterized by the fact that the polyester mixture contains a modifier to adjust the flow properties, viscosity and bank formation of the thermoplastic melt, which is a methacrylate-butadiene-styrene core-shell copolymer or a methacrylate-butyl acrylate core-shell copolymer that is added to the polyester mixture in an amount from 5 to 40 wt%, preferably 10 to 30 wt% in reference to the total weight of the mixture.

[0008] An amorphous polyester polymer that can be processed below 240°C is preferably used as polyester according to a).

[0009] The calenderable polyester mixture according to the invention has the advantage that the thermoplastic melt exhibits good flow properties, which permits a uniform, homogeneous distribution of the melt over the entire roll width without adversely affecting the adhesion behavior of the melt on the calendering rolls during transfer of the melt into the calender nip and formation of the bank (also referred to as **Knet** [in German - translator]) in the roll nip. The formation of folds and waves in the bank is largely ruled out because of the improved flow properties of the melt and the effect of overlapping flows in the roll nip on bank formation is compensated. The uniformly rolling bank that forms in the roll nip on this account largely rules out fluctuations in layer thicknesses and therefore quality deficiencies of polyester films produced on calenders.

[0010] The mixture according to the invention also has higher elongation and viscosity properties, which have a positive effect on bank formation, on the one hand, and on quality of the finished products, on the other.

[0011] It is also advantageous that production disturbances and the related quality deficiencies or shutdowns because of defective bank formation in the roll nip are limited to a minimum.

[0012] The invention is further explained below with reference to a practical example.

### Practical example

[0013] Experiments with thermoplastic, saturated polyester form the basis of the example. Glycol-modified polyethylene terephthalate (PETG), which is permanently amorphous and has a processing range from 150 to 220°C, was used as polyester for the mixture.

[0014] Amorphous polyester PETG, antiblock additives, additives to reduce adhesion and a modifier to ensure the required flow and elongation properties, as well as viscosity of the melt, were mixed together in different mixing ratios to produce the calenderable polyester mixture. The polyester mixture with the additives and the modifiers was predried at 65°C for 4 hours in a dry-air dryer. Compounding then occurred in an extrusion system. Predrying can be omitted, if the processing temperature is low, no water contact occurs during extrusion compounding or the masterbatch is sent directly to the calender. Dry raw materials are a prerequisite.

[0015] The mixing ratios of the individual components are shown in Table 1. The following were mixed:

- (1) Amorphous polyester from Eastman Chemical
- (2) Extrusion antiblock additive from Clariant with about 85% Estar PETG 6763
- (3) Methylacrylate-butadiene-styrene core-shell copolymer from Rohm & Haas
- (4) Calcium stearate lubricant from Henkel

**Table 1.**

Formula//parts by weight	A	B	C
Estar PETG 6763 (1)	60	40	70
Antiblock PETG 191378	25	40	—
Paraloid BTA 702 S	15	20	30
Stalo M 200	0.2	—	0.2

[0016] The modifiers according to the invention based on methacrylate-butadiene-styrene (MBS) or methacrylate-butyl acrylate-(acrylate) core-shell copolymers cannot be characterized with the usual thermoplastic test methods. The following methods were used for this.

**Press flow**

[0017] To determine the residual thermoplasticity, the powders or granulates of the modifiers were pressed under fixed conditions and the thickness determined within the first flow line.

Conditions: 190°C; 50 bar (120 N/m<sup>2</sup>); 30 g of sample

Target thickness: MBS types 1.00 to 1.60 mm, preferably 1.15 to 1.50 mm

Acrylate types 1.04 to 1.12 mm, preferably 1.05 to 1.10 mm

**Torque rheometer**

[0018] To determine the residual thermoplasticity the powders or granulates of the modifiers were kneaded under fixed conditions and the equilibrium torque (Md) determined after 8 to 10 minutes.

**Conditions**

[0019] 165°C; 10 minutes; sample amount 40 g in MBS copolymers and 45 g in acrylate copolymers; standard kneading chamber 69 mL with roll rotors.

Target equilibrium torque:

MBS types 5 to 16 Nm, preferably 10 to 15 Nm

Acrylate types 5 to 13 Nm, preferably 10 to 13 Nm

[0020] The suitable or unsuitable modifiers used as examples gave the following test values shown in Tables 2 and 3 in 100% form.

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**Table 2.**

MBS types (Paraloid)

Modifier	BTA 702 S	BTA 780 S	YC 3-03.05	BTA 736 S
Press flow thickness (mm)	1.41	1.42	1.16	1.67
Equilibrium torque (Nm)	14	14.3	14.1	16.3
Bank formation	+	+	+	–

**Table 3.**

Acrylate-(MMA/BA) types (Paraloid; 1) = Evaloy

Modifier	HIA 80	KM 355	EXL 3300	EXL 2314	K 125	K120 ND	K 175	PTW 1)
Press flow thickness (mm)	1.09	1.07	1.2	1.13	1.03	0.84	0.55	0.48
Equilibrium torque (Nm)	11.3	12.9	13.1	14	23.7	13.9	0.6	2.9
Bank formation	+	+	–	–	–	–	–	–

"+" means the modifier is suitable and "–" means the modifier is unsuitable in Tables 2 and 3.

[0021] The polyester-additive-modifier mixtures are calendered to films, for example, with a thickness of 250  $\mu\text{m}$ , using a measuring roll stand from Dr. Collin GmbH. The results of the modifiers on the example of formula A with good roll behavior are summarized in Table 4 and those with inadequate roll behavior in Table 5.

Table 4.

Formula No.	Modifier	Adhesion, %	Bank score	Film score	Md (Nm)	Bearing force (kN)
A1	Paraloid BTA 702 S	16	1	2	130	11.2
A2	Paraloid BTA 780 S	11.1	1	2	130	11
A3	Paraloid YC 3.03.05	5.5	1-2	2	145	9
A4	Paraloid HIA 80	12.1	1	2	99	7.3
A5	Paraloid KM 355	6.6	1-2	2	99	8.3

Table 5.

Formula No.	Modifier	Adhesion, %	Bank score	Film score	Md (Nm)	Bearing force (kN)
A1	Paraloid BTA 736 S	10.5	2	4	143	12
A2	Paraloid K 125	—	3	6	—	—
A3	Paraloid K 175	—	4	5	47	3.4
A4	Paraloid K 120 ND	—	5	6	—	—
A5	Evaloy PTW	tearing	5	6	58	3.9

[0022] Examples A1 to A5 demonstrate the calenderability of polyesters during achievement of a uniformly forming and rotating bank in the calender nip and therefore the achievement of uniform polyester layers by means of the addition of the modifiers according to the invention based on methacrylate-butadiene-styrene (MBS) or methacrylate-butyl acrylate-(acrylate) core-shell copolymers.



### Claims

1. A calenderable polyester mixture for the production of polyester films, sheets and coatings containing:
  - a) a polyester based on at least 80 mol% of a dicarboxylic acid component, chosen from terephthalic acid, naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, isophthalic acid or their mixtures and at least 80 mol% of a diol component, chosen from diols having 2 to 10 carbon atoms and their mixtures, the polyester having a crystallization half-life in the molten state of at least 5 minutes,
  - b) an additive to reduce adhesion of the polyester; like lubricants, slip agents and antioxidants,
  - c) a crosslinking agent and
  - d) additional modifiers and ordinary additives, **characterized by the fact that**
  - e) a modifier to adjust the flow properties, viscosity and bank formation of the thermoplastic melt, is a methacrylate-butadiene-styrene core-shell copolymer or a methacrylate-butyl acrylate core-shell copolymer, which is added to the polyester mixture in an amount from 5 to 40 wt%, in reference to its total weight.
2. The calenderable polyester mixture according to Claim 1, characterized by the fact that the modifier is preferably added to the polyester mixture in an amount of 10 to 30 wt%.
3. The calenderable polyester mixture according to Claims 1 and 2, characterized by the fact that a polyester polymer of the amorphous type processable below 240°C is preferably used as polyester a).